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## SPECIFICATION

### METHOD FOR CONTROLLING MELT AND METHOD FOR GROWING CRYSTAL

#### Technical Field:

The present invention relates to a method for controlling a melt, particularly to a crystal growing method for use in growing a crystal.

#### Background Art:

Usually, when a crystal is produced from a melt, it is necessary to control a phase mode of the melt, since such a phase mode will often bring about an inference to the physical properties of a grown crystal. Further, there have been known various methods which can be used to control the concentrations of impurities contained in a crystal or can be employed to improve the uniformity of impurity concentrations.

For example, when a quartz crucible is used to produce a crystal from a melt contained in the quartz crucible, there will occur four kinds of phenomena which can be described as follows. ① A first phenomenon is that along an interface between the quartz crucible ( $\text{SiO}_2$ ) and Si melt, the quartz ( $\text{SiO}_2$ ) will be melted so as to mix into the Si melt. ② A second phenomenon is that a concentration gradient existing within the melt will cause a diffusion and a melt flow so that the quartz component will move throughout the melt. ③ A third phenomenon is that ( $\text{SiO}$ ) will be evaporated from a crystal growing interface into an atmosphere hanging above it. ④ A fourth phenomenon is that ( $\text{SiO}$ ) will be evaporated from the surface of the

melt into the surrounding atmosphere. In fact, there has been in test a control for controlling the distribution of an oxygen concentration by virtue of the above four phenomena, as well as a horizontal magnetic field, a vertical magnetic field and a cusped magnetic field.

Furthermore, in order to inhibit an undesired influence caused due to a buoyancy convection, there has been suggested and thus known a method which is effective for providing a rotation to the melt so as to keep the melt under a reduced gravity. In addition, for other purpose than inhibiting the buoyancy convection, for example, for the purpose of dealing with a convection caused due to a surface tension, i.e., for dealing with Marangoni convection, there has been suggested and thus known another method which can be used to optimize the shape and size of a melt, a temperature difference within the melt, as well as an atmosphere condition.

On the other hand, as to the control of a melt for controlling its oxygen concentration, a further method has been suggested in Japanese Unexamined Patent Publication (JP-A) No. 7-291783. In detail, the method disclosed in JP-A No. 7-291783 has suggested that in order to increase an oxygen concentration within silicon (FZ silicon), a number of ring-like oxygen supplying members be provided to a melting zone of a silicon single crystal during a crystal growing process. Further, according to JP-A No. 7-291783, the Floating Zone method (FZ method) can be used to enable a quartz plate to get continuous contact with the front end of a melt so as to form a single crystal, while an oxygen concentration in the edge portions of the single crystal is increased so as to be higher than that in its central portion.

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However, when the ring-like oxygen supplying members or the quartz plate are directly used, the entire area of a silicon single crystal will be associated with a problem that an oxygen concentration distribution is not uniform over the entire area, and another problem that the oxygen concentration is difficult to control. As a result, a silicon single crystal thus formed can not be used as a substrate material for a high quality device. On the other hand, even if it is allowed to select and use only an area of each Si wafer whose impurity concentration is uniform, this will however cause an increase in the production cost, making it difficult for device properties to have a high reliability.

As may be clearly understood from the above discussion, the above-described conventional melt control method is associated with the following problem. Namely, a striation phenomenon represented by so-called impurity stripes, i.e. an ununiform distribution of impurity concentration within the crystal will occur remarkably. Actually, such kind of striation can be detected by virtue of an etching treatment using an etching liquid having a composition of  $H_2SO_4 : H_2O_2 = 5 : 1$ . However, such an etching treatment is carried out only after a mirror-polishing treatment (passing through the center axis of the crystal) has been conducted on each wafer.

In this way, the above-described conventional melt control method has been proved to be extremely difficult in removing the striation which are in fact impurity stripes occurred within the resulting crystal. In other words, the striation phenomenon means that there is an irregular temperature fluctuation within the melt, while the conventional melt control method has been proved to be extremely difficult in prohibiting such an irregular temperature fluctuation which is extremely unfavorable

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for ensuring a uniform crystal growth.

It is an object of the present invention to provide an improved melt control method and an improved crystal growing method, capable of inhibiting an irregular temperature fluctuation within the melt.

Disclosure Of the Invention:

An improved melt control method according to the present invention characterized in that this method is used in controlling the state of a melt covered by a predetermined atmosphere, and that the state of one component of a specific element contained in the atmosphere is controlled to be in a predetermined state. The improved melt control method can be used to effect a crystal growth using the Czochralski method. Further, the melt control method can also be used to perform another crystal growth using the Floating Zone method.

Brief Description of the Drawings:

Fig. 1 is an explanatory view schematically showing an example of a system according to the present invention, involving the use of the FZ method.

Fig. 2 provides the Fourier spectrums showing an oxygen partial pressure of the surrounding atmosphere, as well as a temperature vibration, which spectrums may be used in the system shown in Fig. 1.

Fig. 3 is an explanatory view schematically showing an example of a system according to the present invention, involving the use of the CZ method.

Fig. 4 is a graph showing how an introduced oxygen partial pressure has an effect (influence) on the flow rate in the system shown

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in Fig. 3.

Figs. 5A and 5B are graphs showing how an introduced oxygen partial pressure has an effect (influence) on a convection mode of the melt in the system shown in Fig. 3.

Fig. 6 is a graph showing a relation between an introduced oxygen partial pressure and an oxygen concentration within the Si crystal, which relation is existing in the system shown in Fig. 3.

Fig. 7 provides graphs showing how an introduced oxygen partial pressure has an effect (influence) on a temperature vibration mode in the system shown in Fig. 3.

Fig. 8 is a graph showing a relation between an introduced oxygen partial pressure and a surface oxygen partial pressure, which relation is existing in the system shown in Fig. 3.

#### Best Mode for Embodying the Invention:

The present invention will be described in detail below in accordance with several examples.

At first, description will be given to explain an example which shows that the present invention can be applied to the Floating Zone method (FZ method). In the FZ method, for example, a partial pressure of oxygen acting as one of several components constituting an atmosphere surrounding Si melt is controlled so that it is maintained at 1.8 E (-5) MPa, thereby inhibiting the Marangoni convection usually caused by a surface tension. In this way, a temperature vibration of the melt can be in a single frequency mode, resulting in the formation of a crystal having a high quality and a high homogeneity.

Referring to Fig. 1, a system using the FZ method comprises a high purity argon gas bomb 1 and an Ar-10%O<sub>2</sub> bomb 4. A high purity argon gas is supplied through a mass flow controller 2a into a gas refining apparatus 3 to remove impurities. On the other hand, with the use of another mass flow controller 2b, an argon-based oxygen doping gas and an Ar-10%O<sub>2</sub> gas flowing from the Ar-10%O<sub>2</sub> bomb 4 are precisely controlled. Thereby, the argon-based oxygen doping gas and the Ar-10%O<sub>2</sub> gas are added into the high purity Ar gas by way of a gas pipeline 15.

In this way, an argon-based oxygen formed by mixing the high purity Ar gas with the Ar-10%O<sub>2</sub> gas, is caused to flow through a valve 6a and branched into two mass flow controllers 2c and 2d. The argon-based oxygen is supplied from the mass flow controller 2c into an FZ image furnace (an infrared image furnace) 8. On the other hand, in order to measure an oxygen partial pressure 10 in the atmosphere, the argon-based oxygen is supplied through a further mass flow controller 2d to an oxygen sensor 7. Here, such an oxygen sensor 7 is so constructed that it can operate by virtue of an electro motive force generated by an oxygen concentration battery. In practice, such an oxygen partial pressure measurement can be carried out by using a zirconia-containing solid electrolyte oxygen sensor which is capable of conducting oxygen ions at a temperature of 800°C, while its reference electrode is formed by a powder mixture containing Ni and NiO. In addition, the oxygen sensor 7 is so formed that it can obtain an electro motive force corresponding to an activity difference.

Moreover, in order to precisely control an oxygen partial pressure in the atmosphere, a magnesium (Mg) deoxidizing furnace 5 is

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connected to the pipeline 15 through another two valves 6b and 6c, so that an atmosphere gas can be introduced into the magnesium (Mg) deoxidizing furnace 5. Here, such a magnesium (Mg) deoxidizing furnace 5 is so constructed that it can operate by making use of a chemical equilibrium between a metal magnesium and its oxide.

Namely, the magnesium (Mg) deoxidizing furnace 5 may be formed by, for example, filling an electric resistance furnace with 500 g of a metal magnesium so that when the temperature of the furnace is controlled, it is possible to precisely control the partial pressure of oxygen contained in the atmosphere, by making use of a deoxidizing effect produced by the metal magnesium.

In this way, as described in the above, an oxygen partial pressure can be controlled continuously and such an oxygen partial pressure can be measured in a real time base. At this time, an amount of silicon melt 11 can be produced under the controlled oxygen partial pressure using the FZ image furnace 8. As shown in the drawing, an auxiliary heater 16 is provided within the FZ image furnace 8. With the use of the auxiliary heater 16, a desired temperature difference may be formed within the silicon melt.

Then, in the silicon melt prepared in the above manner, several thermal couples 9 each having a diameter of  $\phi 0.1$  mm were used to precisely measure a temperature vibration of the silicon melt.

Moreover, a vacuum pump 12 is connected through a valve 6d to the FZ image furnace 8, while the oxygen sensor 7 is connected to a personal computer 13 through a digital volt meter (DVM) 14a. Further, the personal computer 13 is connected with the thermal couples 9 by another digital volt meter (DVM) 14b. In this way, an oxygen partial

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pressure and a temperature vibration can be displayed on the personal computer 13.

Next, Fig. 2 will be used to explain the results of the Fourier analysis for analyzing a temperature vibration under a condition in which an oxygen partial pressure has been controlled. In fact, the Fourier analysis is conducted from area I (PHASE 1) to area IV (PHASE IV).

As may be clearly understood from Fig. 2, when a temperature difference between upper and lower portions of the silicon melt is  $\Delta TL = 52K$ , an area II having a low oxygen partial pressure (oxygen partial pressure  $PO_2 = 3.5 \times 10^{-7}$  MPa) has a plurality of cycles of temperature fluctuations. On the other hand, another area I having an oxygen partial pressure  $PO_2 = 9.0 \times 10^{-6}$  MPa, is associated with a temperature vibration trending to have a cycle in the vicinity of a frequency of 0.20 Hz, thus proving that it is not a temperature vibration having a pure single cycle. However, with regard to an area III having an increased oxygen partial pressure (an oxygen partial pressure  $PO_2 = 1.8 \times 10^{-5}$  MPa), it was first found that this area has a clear single cycle of 0.70 Hz. Further, an area IV where a temperature difference between upper and lower portions of the silicon melt is  $\Delta TL = 48K$ , and an oxygen partial pressure  $PO_2 = 7.5 \times 10^{-6}$  MPa, it was first found that a temperature vibration having two cycles 0.65 Hz and 0.20 Hz are modulated.

The reason for the above phenomenon can be elucidated by explaining a convection caused due to a surface tension, i.e., by explaining a relational expression containing the Marangoni convection.

The intensity of the convection caused by the surface tension, i.e., the intensity of the Marangoni convection can be represented by a

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dimensionless Marangoni number which is

$Ma = (|\partial\gamma/\partial T|) \Delta TL / \mu \kappa$ . Here,  $\partial\gamma/\partial T$  is a temperature coefficient of surface tension, L is a representative length of a melt,  $\mu$  is a viscosity coefficient, and  $\kappa$  is a thermal diffusion coefficient.

As may be understood in the above relational expression, the Marangoni number is dependent on a temperature coefficient of surface tension. Namely, a surface tension and a temperature coefficient of a silicon melt are all dependent on an oxygen partial pressure of the surrounding atmosphere. In addition, it is possible to predict that the larger the oxygen partial pressure is in the atmosphere, the smaller the temperature coefficient of surface tension  $\partial\gamma/\partial T$  will be. The vibration mode of the Marangoni convection, with an increase in the Marangoni number in the system, will transit in a manner of constant flow → cyclic vibration flow → non-cyclic vibration flow.

Further, as indicated in Fig. 2, when an oxygen partial pressure is increased, a plural-cycle vibration will gradually transit to a single-cycle vibration. This is because when an oxygen partial pressure in the atmosphere has been increased, an oxygen adsorption will occur due to a chemical equilibrium in the silicon melt, so that the temperature coefficient of surface tension of the silicon melt will be decreased. In this way, it becomes possible to inhibit the intensity of the Marangoni convection usually caused due to the surface tension.

As shown in the above example, by controlling the oxygen partial pressure in the surrounding atmosphere, it becomes possible that if the physical properties of a melt including the viscosity coefficient  $\mu$  and the thermal diffusion coefficient  $\kappa$  are all kept constant, not only the temperature coefficient  $\partial\gamma/\partial T$  of surface tension (which is one

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parameter of the oxygen partial pressure), but also other two parameters (including an upper/lower temperature difference  $\Delta T$  and a melt liquid column length L), can be under the control of the Marangoni number  $Ma$ , thus ensuring a single cycle for Marangoni convection mode.

Next, description will be given to explain an example which shows that the present invention can be applied to the Czochralski method (CZ method). In the following example involving the use of the CZ method, the partial pressure of oxygen acting as one of several components constituting an atmosphere surrounding Si melt is controlled. Particularly, an introduced oxygen partial pressure is controlled so as to inhibit the Marangoni convection. In this way, it is possible to stabilize the melt flow so as to control effectively the oxygen concentration within the crystal, thereby effecting the growth of a single crystal having a high quality. Further, if an introduced oxygen partial pressure is increased, a temperature vibration of the melt can be in a single frequency mode, resulting in the formation of a crystal having a high quality and a high homogeneity.

Referring to Fig. 3, a system for carrying out the CZ method involves the same essential elements as used in the system shown in Fig. 1. Thus, the same essential elements as used in the above are represented by the same reference numerals. In detail, the system for carrying out the CZ method includes CZ image furnace 21. Then, in the same manner as shown in Fig. 1, the mass flow controller 2c is operated to supply an argon-based oxygen (formed by mixing together a high purity Ar gas and an Ar-10%O<sub>2</sub> gas) to the CZ image furnace 21, while at the same time controlling an oxygen partial pressure to a

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predetermined value. On the other hand, in order to measure an oxygen partial pressure 22 in the atmosphere within the CZ image furnace 21, the argon-based oxygen is supplied through a further mass flow controller 2d to an oxygen sensor 7.

As shown in the drawing, the CZ image furnace 21 is equipped with a rotating shaft 26. A melt holding member 25 is supported on the rotating shaft 26. Further, a heater 24 is arranged around the melt holding member 25. Therefore, an amount of silicon melt 11 may be held by the melt holding member 25 during the process of forming a silicon crystal 23, as will be described in detail later.

Further, in this example shown in the drawing, the melt holding member 25 contains an amount of carbon material. Usually, a melt holding member for drawing-up a silicon melt contains a quartz glass. Here, using a carbon material in the melt holding member is only for the purpose of forming a melt holding member not containing an oxygen source so as to verify an effect of the oxygen partial pressure 22 in the atmosphere. However, when an oxygen partial pressure in the atmosphere is controlled in order to control an oxygen concentration, it will be proved to be effective if the melt holding member contains a nitride such as BN (boron nitride) and ALN (aluminum nitride) besides the carbon material.

Moreover, a vacuum pump 12 is connected to the CZ image furnace 21, while the oxygen sensor 7 is connected to a personal computer 13 through a digital volt meter (DVM) 14a. In this way, an oxygen partial pressure and a temperature vibration may be displayed on the personal computer 13.

In the system shown in Fig. 3, Si melt 11 was formed and an

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upper/lower (upper surface and bottom surface) temperature difference in Si melt 11 was set to be 50 K, so that a ratio of the melt radius to the melt height became 1:1. Further, when an oxygen partial pressure 22 in the atmosphere was in a range of  $1.0 \times 10^{-8}$  to  $1.0 \times 10^{-4}$  MPa, an amount of tracer particles ( $ZrO_2$  zirconia,  $\phi 450 \mu m$ ) were inserted on to the surface of the silicon melt 11 to measure the flow rate, so as to make clear an effect (an influence) of the oxygen partial pressure 22 on the flow rate of the Marangoni convection. Fig. 4 shows the results of the measurement.

As may be understood in Fig. 4, when an introduced oxygen partial pressure (an oxygen partial pressure in the atmosphere) is increased, the flow rate of the tracer particles will be reduced. This means it is allowed to make use of a fact that the oxygen partial pressure depends on the flow rate of the tracer particles, so at it is possible to control the flow rate of the Marangoni convection, with the introduced oxygen partial pressure being used as one control parameter.

Here, Figs. 5A and 5B are used to show the trace of the tracer particles, illustrating different flow structures. Here, it is understood that when an introduced oxygen partial pressure is  $1.0 \times 10^{-6}$  MPa, the trace of the flow will have a relatively complex 3-dimensional structure (Fig. 5A). On the other hand, when an introduced oxygen partial pressure has been increased to  $1.0 \times 10^{-4}$  MPa, the trace of the flow will become axially symmetrical (Fig. 5B). Then, if the flow rate of the Marangoni convection on silicon surface is reduced and a flow towards the inner portion of the silicon melt is inhibited, a phase transition of the convection mode will occur.

Fig. 6 is a graph which can be used to indicate a relation between

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an introduced oxygen partial pressure and an oxygen concentration in the crystal. As can be understood in Fig. 6, controlling an oxygen partial pressure in the atmosphere makes it possible to control an oxygen concentration in the crystal.

Fig. 7 is used to indicate a relation between an introduced oxygen partial pressure and a temperature vibration. As already explained earlier in relation to Fig. 1, it can be understood that an area having a relatively high oxygen partial pressure 22 in the atmosphere (an introduced oxygen partial pressure  $P_{O_2} = 1.8 \times 10^{-5}$  MPa), has a clear single cycle of 0.70 Hz. This fact can be explained properly by using a relational expression of the Marangoni convection.

Further, as already discussed earlier in relation to Fig. 1 and Fig. 2, the Marangoni number depends on the temperature coefficient of surface tension, while vibration mode of the Marangoni convection, due to an increase in the Marangoni number, will have a transition which can be represented as: constant flow  $\rightarrow$  cyclic vibration flow  $\rightarrow$  non-cyclic vibration flow.

As shown in Fig. 7, once an oxygen partial pressure is increased, a plural-cycle vibration will be transited to a single-cycle vibration. This is because when an oxygen partial pressure has been increased, an oxygen adsorption due to a chemical equilibrium will occur in the silicon melt, thereby rendering the silicon melt to reduce its temperature coefficient of surface tension. As a result, it is possible to inhibit the intensity of the Marangoni convection which is in fact a convection usually caused by the surface tension.

In addition, the control of an oxygen partial pressure in the atmosphere can be effected in the same manner as shown in Fig. 1 and

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Fig. 2. Namely, if the physical properties of the melt are all kept constant, not only the temperature coefficient  $\partial \gamma / \partial T$  of surface tension (which is one parameter of the oxygen partial pressure), but also other two parameters (including an upper/lower temperature difference  $\Delta T$  and a melt liquid representative length), can be under the control of the Marangoni number  $Ma$ , thus ensuring a single cycle for the Marangoni convection mode.

However, in the system of Si (melt) - O<sub>2</sub> (gas), since the vapor pressure of SiO gas ( $P_{SiO}^{VAP}$ ) is 1.7 E (-4) MPa which is larger than the vapor pressure of Si liquid ( $P_{Si}^{VAP}$ ) which is 3.8 E (-8) MPa, introduced oxygen molecules will react (as SiO gas) instantly with the oxygen molecules remaining on the surface of Si melt. For this reason, it is allowed to consider that an oxygen partial pressure on the surface of the silicon melt will become lower than an introduced oxygen partial pressure. Further, since there is a reaction between Si (liquid) and O<sub>2</sub> (gas) by virtue of a chemical equilibrium, a saturated oxygen partial pressure produced by SiO<sub>2</sub> (solid) at a temperature of 1693 K is 1.3 E (-20) MPa.

In the experiments conducted by the inventors of the present invention, when an introduced oxygen partial pressure was 1.0 E (-4) MPa, the silicon melt could be found to have a free surface. On the other hand, when an introduced oxygen partial pressure was only slightly larger than 1.0 E (-4) MPa, it was found that SiO<sub>2</sub> (solid) precipitation began to occur.

Moreover, it was clearly understood that when an introduced oxygen partial pressure is 1.0 E (-2) MPa, the Marangoni convection within the silicon melt will not be found, while the surface thereof will be

covered by  $\text{SiO}_2$  (solid).

Thus, it can be understood from the above results that when an introduced oxygen partial pressure is in a range of  $1.0 \times 10^{-4}$  MPa to  $1.0 \times 10^{-2}$  MPa, a saturated oxygen partial pressure will exist on the surface of the silicon melt. Fig. 8 is a graph which shows a relation between an introduced oxygen partial pressure and a surface oxygen partial pressure (formed by virtue of an extrapolation), based on the results of the above observations. As shown in the graph, when an introduced oxygen partial pressure is  $1.0 \times 10^{-4}$  MPa, the surface oxygen partial pressure will be  $9.6 \times 10^{-22}$  MPa. Further, during the temperature vibration, it is allowed to predict that an introduced oxygen partial pressure in a single-cycle formation process will be  $1.8 \times 10^{-5}$  MPa, while a surface oxygen partial pressure will be  $3.1 \times 10^{-23}$  MPa.

Therefore, when an oxygen partial pressure to be introduced is controlled so as to control the Marangoni convection, the surface oxygen partial pressure will be in a range not higher than a saturated oxygen partial pressure formed in accordance with a chemical equilibrium theory. Namely, if a free surface of the silicon melt is existing and the Marangoni convection is controlled by controlling an introduced oxygen partial pressure, or the surface oxygen partial pressure is used as a parameter to control a flow mode, it is possible to grow a single-crystal having a high quality.

As described in the above, using an oxygen partial pressure makes it possible to freely control the Marangoni convection of a silicon melt. This fact may be used as a new process parameter for growing silicon crystal, using the CZ method which is suitable for producing crystal having a diameter of 400 mm, and it can also be used in

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numerical value simulation technology for general heat transfer analysis.

Although the above examples have been described in which the melt is Si, the principle of the present invention can also be applied to the case where a melt is a semiconductor, a metal or a polymer, without having to limit the melt to the material used in the above examples. In fact, when a melt is formed by a material which is not Si, a component for use in controlling a partial pressure should not be limited to oxygen.

Advantages of the Invention:

As described in the above, with the use of the present invention, it has become possible to effectively inhibit some buoyancy convections other than the Marangoni convection. For example, in the crystal growth Floating Zone method (FZ method), the temperature vibration within a melt will become a single-cycle vibration, while a turbulence of the temperature vibration will disappear, thereby forming a crystal having a high homogeneity.

Furthermore, even in the crystal growth Czochralski method (CZ method), controlling an oxygen partial pressure makes it possible to control the Marangoni convection on the surface of the silicon melt. In this way, the temperature vibration of the melt flow will be in a single cycle, the turbulence of the temperature vibration will disappear, and it is possible to form a uniform distribution of the oxygen concentration. As a result, it becomes possible to obtain an effect of providing a crystal having a high quality. In addition, it is also possible to control the oxygen concentration in the crystal, using the oxygen partial pressure as one control parameter.

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